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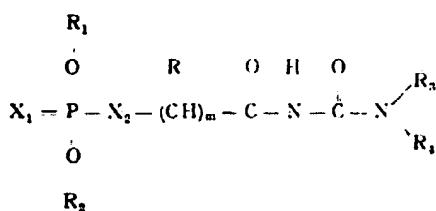
Method for the Manufacture of Esters of the Phosphoric or Thiophosphoric Acid

Patented in the region of the Federal Republic of Germany since 13 May 1949

The granting of the patent was announced on 26 April 1951

Priority of the application in the United States of America of 5 June 1948 has been claimed

This invention pertains to a method for the manufacture of esters of the phosphoric or thiophosphoric acid, with the genera formula of



in which X₁ and X₂ are sulfur or oxygen atoms,

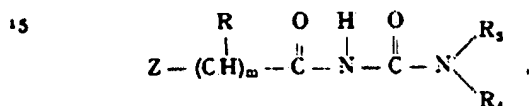
R is a hydrogen atom or an alkyl, R₁ and R₂ are 15
alkyls, aralkyls, cycloalkyls or aryls, R₃ and R₄ are
hydrogen atoms, alkyls or aryls, and m is a small
integer number.

In the new compounds, R₁ and R₂ can be equal 20
or different moieties and, if they are alcyly, may
exhibit straight or complex chains, may be of
saturated or unsaturated nature, and may also
contain halogen substitutes, especially chlorine and 25
bromine. Typical samples of such moieties are methyl,
ethyl, n-propyl, isopropyl, isobutyl, sec. amyl, n-hexyl,
2-ethylhexyl, n-octyl, n-decyl, n-dodecyl,

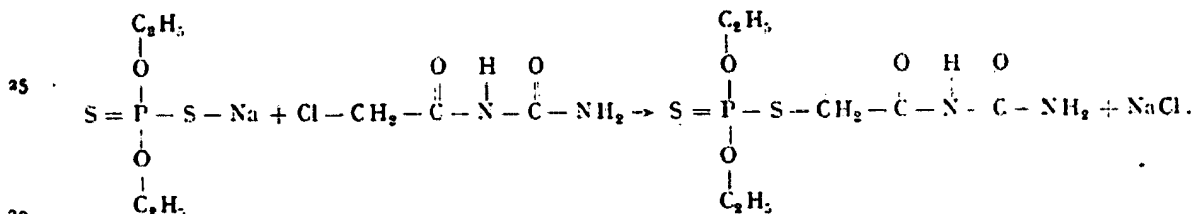
oleyl, cetyl, ceryl, allyl, bromine methyl, 2-chlorine ethyl, cyclohexyl, benzyl, phenyl, p-chlorophenyl, o-, m- and p-nitrophenyl moieties.

5 The compounds in this invention are used as pesticides and exhibit insecticidal, rodenticidal and fungicidal properties. They can also be used to prevent corrosion, as softeners, flotation devices and petroleum additives.

10 These esters of the phosphoric or thiophosphoric acid are the result of the transformation of halogen acyl urea with the general formula

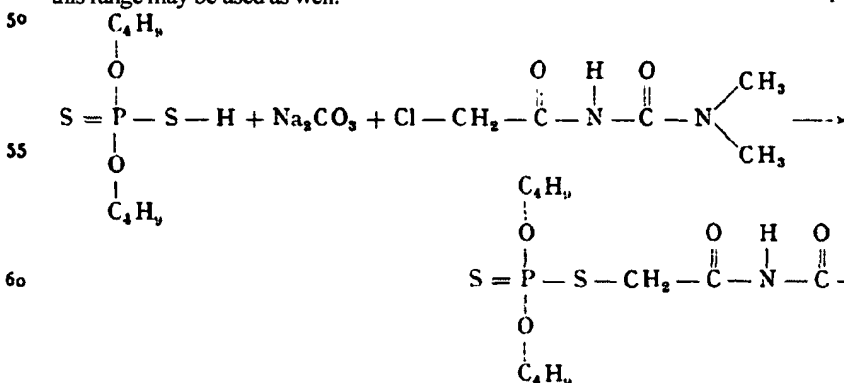


20 in which Z represents chlorine or bromine atoms, and R, m, R₃ and R₄ have the indicated meaning

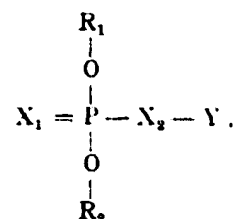


30 High yields of the desired products are achieved, when the transformation takes place in the presence of a solvent. Such solvents are water, low-molecular, aliphatic, monovalent types of alcohol, ketones, e.g. acetone, methylethylketone, methylisobutylketone, methylbenzylketone, cyclohexanon, acetophenon etc., aliphatic esters, like ethylacetate, amylacetate, m-ethylhexylacetate, methylpropionate, methylbutyrate, ethylbutyrate, and isopropylbutyrate; 40 saturated aliphatic nitriles like acetonitrile and propionitrile; dioxane, nitrobenzene, chlorobenzene, toluene, xylol, chloroform, carbon tetrachloride, 1,2-dimethoxyethane and trialkylphosphates like tri-methylphosphate, triethylphosphate and triisopropylphosphate.

45 The ideal temperature for the transformation is 20 to 150 °C. However, depending on the type of the reacting substances and the solvents being used, temperatures outside this range may be used as well.

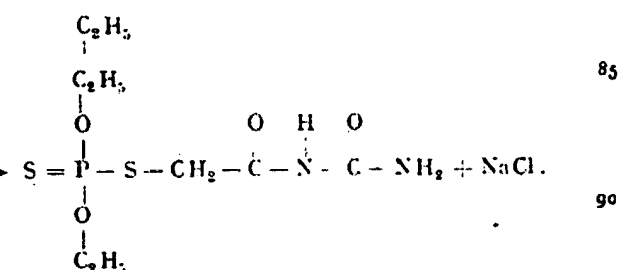


with a phosphate or thiophosphate of the general formula



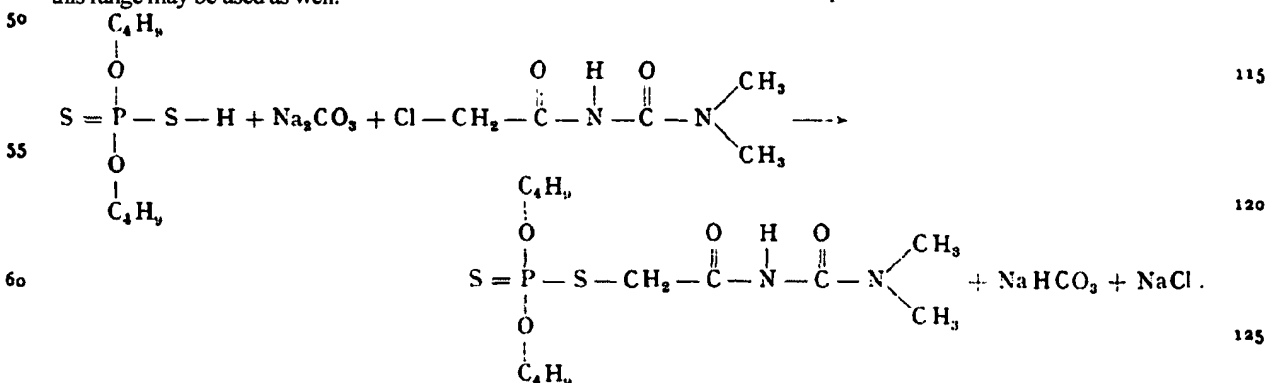
75 in which Y is an alkali metal or alkaline earth metal or the NH₄ moiety, and the meaning of X₁, R₁, R₂ and X₂ is as indicated.

A typical sample reaction, in which sodium-o,o-diethyldithiophosphate reacts with chloroacetylurea for the creation of dithiophosphoric acid-o,o-diethylester-S-ureidocarboylmethylester can be illustrated as follows:



90 A slightly modified embodiment of the invention uses in the place of the alkaline phosphate or the thiophosphate-ester the corresponding acid and an alkaline cationation of the alkaline metal, whereby the alkalinity of the latter must be sufficient enough to neutralize said acid. This method avoids the initial creation and isolation of the alkali-phosphate- or thiophosphate-ester. Such alkaline compounds are sodium carbonate, potassium carbonate, barium carbonate, magnesium carbonate, lithium carbonate, sodium hydroxide, potassium hydroxide, calcium hydroxide, strontium hydroxide, magnesium hydroxide, sodium hydrosulfide, sodium borate, tri-potassium arsenite, sodium pyrophosphate, barium phosphate, tri-sodiumphosphate, etc.

105 If the method named above is used for the creation of dithiophosphoric acid-o,o-di-n-butylester-S-dimethylureidocarboylmethylester, the reaction can be represented as follows:



The halogenacylureas being used in the creation of the compounds according to this invention are known and are manufactured by generally known methods, e.g. chloroacetylurea is the result of the reaction of chloroacetyl chloride with urea.

The following embodiments, in which the parts represent weights, explain the invention further.

Embodiment 1

50 parts of dithiophosphoric acid-o,o-diethylester (93 proof) were slowly added to a well-agitated mixture of 26.5 parts of anhydrous sodium carbonate suspended in 100 parts of methylisobutylketone. The temperature increased spontaneously to about 40°C. 34.1 parts of chloroacetylurea were slowly added, and the resulting mixture was continued to be agitated and kept at a temperature of 60 to 65°C for 6 hours. The warm reaction mixture was then filtered through a sintered glass funnel. The filtrate was heated under vacuum in order to distill the methylisobutylketone, and for the resulting solid substance of tetrachlorocarbon to recrystallize. The product, dithiophosphoric acid -o,o-dimethylester -S-ureidocarboylmethylester formed a clear, crystalline substance that melted at 93 to 95° C.

Embodiment 2

Using the method from embodiment 1, 43.8 parts of dithiophosphoric acid-o,o-dimethylester (90 proof) were transformed in the presence of 26.5 parts of anhydrous sodium carbonate, 100 parts of methylisobutylketone and 34.1 parts of chloroacetylurea. The product, dithiophosphoric acid-o,o-dimethylester-S-ureidocarboylmethylester formed after recrystallization from carbon tetrachloride a clear, crystalline substance, which melted at 117 to 118 °C.

Embodiment 3

Using the method from embodiment 1, 40 parts of dithiophosphoric acid-o,o-diethylester (93 proof) were converted in the presence of 21.2 parts anhydrous sodium carbonate and 150 parts methylisobutylketone with 44.6 parts a-bromoisovalerylurea. The product, dithiophosphoric acid-o, o-diethylester- S - [(a-ureidocarboyl) - isobutyl]-ester formed after recrystallization from a tetrachlorocarbon mixture (same parts by volume) a clear, crystalline substance that melted at 96 to 97°C.

Embodiment 4

Using the method from embodiment 1, 23.3 parts of dithiophosphoric acid-o,o-diisopropylester (92 proof) were converted in the presence of 11.6 parts of anhydrous sodium carbonate and 75 parts of methylisobutylketone with 15 parts of N-chloroacetyl-N'-methylurea. The result was 31 parts (95% yield) dithiophosphoric acid-o,o-diisopropylester-S-methylureidocarboylmethylester.

After recrystallization from hexane, the product

was a clear, crystalline substance with a melting point of 97 to 98°C.

Embodiment 5

31.9 parts of dithiophosphoric acid-o,o-di-n-amylester (85% proof) were slowly added to a well-stirred mixture of 11.6 parts of anhydrous sodium carbonate, suspended in 100 parts of methylisobutylketone. 13.7 parts of chloroacetylurea were added, and the resulting mixture - while being agitated - was kept at 60 to 70 °C for 3 hours. The reaction mixture was washed three times with water, dried with anhydrous sodium carbonate, and filtered. The methylisobutylketone was removed from the filtrate by vacuum distillation, and left 35 parts (95% yield) of dithiophosphoric acid-o,o-di-n-amylester-S-ureidocarboylmethylester as an oily residue, which quickly hardened into a wax-like solid substance. After recrystallization, first from hexane and then from petroleum ether, the product was a clear, wax-like, solid substance, which melted at 47 to 48 °C.

Embodiment 6

45.5 parts of dithiophosphoric acid-o,o-di-n-decylester (90% proof) were slowly added to a well agitated mixture of 11.6 parts anhydrous sodium-carbonate, suspended in 100 parts methyl isobutylketone. 21.3 parts N-chloroacetyl-N'-phenyl urea were mixed, and the resulting mixture was kept for 8 hours at 60 to 65° C under continued agitation. The reaction mixture was then cooled to room temperature and filtered off. The filtrate was washed three times with water, dried via anhydrous sodium sulfate, followed by the solvent being removed by vacuum distillation.

The resulting product, dithiophosphoric acid-o,o-di-n-decylester-S-phenylureidocarboylmethylester was obtained at 90% yield as an amber-colored, viscous liquid with a refractive index of $n_D^{25} = 1.5222$.

Embodiment 7

A mixture of 20.5 parts of potassium-o,o-diethylmonothiophosphate and 13.5 parts of chloroacetylurea, solved in 75 parts of methylisobutylketone was for 10 hours under constant stirring heated to 60 to 70 °C and then filtered. The filtrate was washed twice with water, dried via anhydrous sodium sulfate, filtered and freed of the solvent by vacuum distillation. The resulting product, monothiophosphoric acid-o,o-diethylester-S-ureidocarboylmethylester was first recrystallized from carbon tetrachloride and then from benzene, and formed a clear, crystalline substance, which melted at 74 to 75 °C.

Embodiment 8

Using the method of embodiment 1, 28.2 parts of dithiophosphoric acid-o,o-diphenylester were

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transformed in the presence of 11 parts of anhydrous sodium carbonate and 100 parts acetone with 13.7 parts chloroacetylurea. The result were 35.4 parts (93% yield) of dithiophosphoric acid-o,o-di-phenylester-S-ureidocarboylmethylester. After recrystallization from benzene, the product formed clear, needle-like crystals, which melted at a temperature of 99 to 100 °C.

Embodiment 9

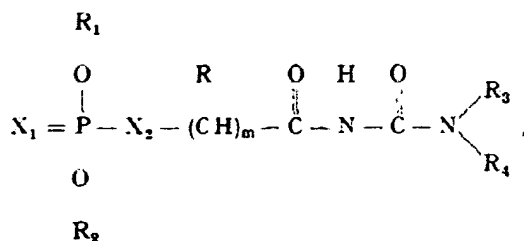
34.6 parts of diethylchlorophosphate in the form of drops were added over a period of one hour to a well-agitated solution of 25.2 parts potassium hydroxide (89%) in 160 parts of ethyl alcohol at 10 to 15 °C. The mixture was kept at 20 to 25 °C for 1 ½ hours, followed by the removal of 90 parts of the ethylalcohol by vacuum distillation. 100 parts acetone and 27.4 parts of chloroacetylurea were added, and the mixture was kept at 25 to 30 °C for 6 hours. The reaction mixture was filtered, and the acetone and the ethyl alcohol were removed from the filtrate by vacuum distillation. The resulting product (48.6 parts; 96% of the yield) phosphoric acid-diethylesterureidocarboylmethylester was a straw-colored liquid with a refractive index of $n_D^{25} = 1.4382$.

The phosphate and thiophosphate esters of this invention can be used as pesticides against some types of insects and mites, e.g. black bean aphids, green peach aphids, pea aphids, chrysanthemum aphids, greenhouse thrips, red Californian scales, red citrus spiders, red greenhouse spiders, silk plant beetles, corn beetles, slaters, cockroaches, procession moth, yellow-fever mosquitos, malaria mosquitos, Mexican bean beetles, and black carpet beetles.

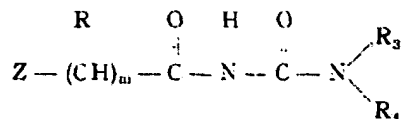
The new compounds can also be used in combination with known insecticides like lead arsenate, nicotine, rotenon, pyrethrum, hexachloro-benzene, 1,1,1-Trichloro-2,2-di-(p-chlorophenyl) ethane, dodecylrhodanide, phenothiazin etc., with fungicides like sulphur, various copper compounds, mercury salts, etc. and with various types of plant foods and fertilizers.

PATENT CLAIMS:

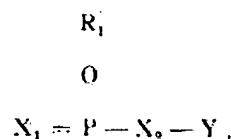
1. Method for the manufacture of esters of the phosphoric or thiophosphoric acid with the general formula



wherein X_1 and X_2 represent sulphur and oxygen atoms, R is a hydrogen atom or an alkyl group, R_1 and R_2 are alkyl, arakyl, cycloalkyl or aryl moients, R_3 and R_4 stand for hydrogen atoms, alkyl or aryl moients, and m is an integer, small number, characterized by the fact that a halogen acyl urea with the general formula



wherein R, m, R_3 and R_4 have the indicated meaning, and Z are chlorine or bromine atoms, is brought to reaction with a phosphate or thiophosphate with the general formula

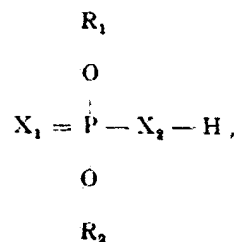


O

R_2

wherein Y is an alkaline or alkaline earth metal or NH_4 moiety, and X_1 , X_2 , R_1 and R_2 have the indicated meaning.

2. Modification of the method according to claim 1, characterized by the fact that the above-named halogen acyl urea reacts with an acidic phosphate of the general formula



wherein X_1 , X_2 , R_1 and R_2 have the indicated meaning, in the presence of an alkaline-reacting alkali-compound, e.g. sodium carbonate, whose alkalinity is sufficient to neutralize the acid phosphate.

3. Method according to claim 2, wherein sodium carbonate is used as an alkaline compound.

4. Method according to claims 1 and 2, wherein the reaction takes place in the presence of a solvent.

5. Method according to claims 1 to 3, wherein the reaction takes place at a temperature of about 20 to about 150 °C.



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December 5, 2006

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